P1 1197855

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office

July 27, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: *60/471,717*
FILING DATE: *May 19, 2003*
RELATED PCT APPLICATION NUMBER: *PCT/US04/15411*

REC'D 30 JUL 2004
WIPO PCT

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

P. R. Grant

P. R. GRANT
Certifying Officer

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

5-20-03 60471717 .051 AVPROV

05/19/03 JC857 U.S. PTO

PTO/SB/16 (11-95)
Approved for use through 01/31/98. OMB 0651-0037
Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(b)(2).

Docket Number	KENT-B-PROV (#245)	Type a plus sign (+) inside this box →	+

INVENTOR(s)/APPLICANT(s)

LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)
CHIEN	Liang-Chy		Hudson, Ohio, U.S.
LAVRENTOVICH	Oleg	D.	Kent, Ohio, U.S.

TITLE OF THE INVENTION (280 characters max.)

APPARATUS AND METHOD OF PLASMA TREATMENT OF THE ALIGNING FILMS FOR LIQUID CRYSTALS

JC857 U.S. PTO 60/471717 05/19/03

CORRESPONDENCE ADDRESS

Daniel J. Hudak
Hudak, Shunk & Farine Co. LPA
2020 Front Street, Suite 307
Cuyahoga Falls, OH 44221 US

STATE	Ohio	ZIP CODE	44221	COUNTRY	U.S.A.

ENCLOSED APPLICATION PARTS (check all that apply)

☒ Specification	Number of Pages 24	☐ Small Entity	
☒ Drawings	Number of Sheets 10	☐ Other (specify)	

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)

☒ A check or money order is enclosed to cover the filing fees. ☒ The Commissioner is hereby authorized to charge any deficiencies or credit any fees to Deposit Account Number: 08-3150	FILING FEE AMOUNT(s)	$160.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No

☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,

SIGNATURE: Daniel J Hudak Date: MAY 19, 2003

TYPED OR PRINTED NAME Daniel J. Hudak REGISTRATION NO. 25,879
(if appropriate)

☐ Additional inventors are being named on separately numbered sheets attached hereto.

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT LAW DEPARTMENT

60471717 .051903

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(b)(2).

Additional Inventors:

Docket Number	KENT-B-PROV (#245)	Type a plus sign (+) inside this box →	+

INVENTOR(s)/APPLICANT(s)			
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)
DOBROVOLSKYY	Andriy		Kyiv, Ukraine
YAROSHCHUK	Oleg		Kyiv, Ukraine

60471717 .051903

CERTIFICATE OF MAILING BY "EXPRESS MAIL" UNDER 37 CFR 1.10 - SEPARATE PAPER

Applicant: Liang-Chy Chien et al.

Serial No.:

For: "APPARATUS AND METHOD OF PLASMA TREATMENT OF THE ALIGNING FILMS FOR LIQUID CRYSTALS"

Examiner: Group Art Unit:

"Express Mail" Label No.: **EV293764370US**

Date of Deposit: **May 19, 2003**

I hereby certify that this paper or fee is being deposited in the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Mail Stop PROVISIONAL PATENT APPLICATION, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Respectfully submitted,

HUDAK, SHUNK & FARINE CO. LPA

Daniel J. Hudak

Daniel J. Hudak
Registration No. 25,879

DJH/lb

2020 Front Street
Suite 307
Cuyahoga Falls, OH 44221-3257
(330) 535-2220

Attorney Docket No.: KENT-B-PROV (#245)

Enclosures:
- Return Postcard
- Express Mail Certificate
- Provisional Patent Application Cover Sheet
- Provisional Patent Application - 24 sheets
- Informal Drawings – 10 sheets
- Filing Fee - check in the amount of $160.00

Attorney Docket No.: KENT-B-PROV (#245)

APPARATUS AND METHOD OF PLASMA TREATMENT OF THE ALIGNING FILMS FOR LIQUID CRYSTALS

FIELD OF INVENTION

The present invention relates to methods of uniform alignment of liquid crystals (LCs). More particularly, this method is based on the treatment of LC aligning substrates with a collimated or partially collimated plasma beam.

BACKGROUND OF THE INVENTION

A uniform surface alignment of liquid crystals (LCs) is an important problem in practical applications of liquid crystal cells. The case of uniform alignment, the direction of the average orientation of LC molecules on the substrate can be described by two angles - zenithal angle θ (the angle between the substrate and the direction of LC average orientation, also called the pretilt angle of the LC, and the azimuth angle φ (the angle in the plane of the substrate, measured between the director and some axis). In absence of external torques, the two angles have well-defined equilibrium values or range of values that are determined by the specifics of molecular interactions at the liquid crystal-substrate interface. These equilibrium values determine one, two, or more "easy axis" or "easy axes" directions. The angle θ can be used to classify the types of uniform alignment of LC. Three cases can be cited:

1) homeotropic (also known as perpendicular or normal) alignment characterized by preferential orientation of LC molecules in a direction normal to the film. In this case LC pretilt angle θ is equal to 90°

2) planar alignment (azimuth) characterized by uniaxial ordering of LC molecules in plane of the aligning substrate (θ equals 0).

3) tilted alignment (zenithal) with the orientation axis obliquely oriented with respect to the aligning substrate. For this type of alignment $0° < \theta < 90°$.

The first type of alignment implies that the azimuth angle φ is not specified, whereas 2) and 3) types are characterized by a well-defined value of the azimuth angle φ.

As a rule, homeotropic alignment of LC can be relatively easy obtained. The most common method is a treatment of the aligning substrates with surfactant materials. In contrast, great skill is required to obtain planar or tilted alignment with desirable alignment parameters. The most common technique for this alignment is a unidirectional rubbing of special aligning films (e.g., polymer films) deposited at the bounding substrates. However, this method often hinders the further improvement of the devices based on LC cells because of several principal drawbacks. The rubbing process causes surface deterioration as well as generation of electrostatic charges and dust on the aligning surfaces. Besides, it is not convenient for the fabrication of LC cells having some special structure, for example, multidomain cells. The reason is that the rubbing method implies mechanical contact with aligning substrates. To avoid the problem, a number of non-contact LC alignment methods has been suggested. Among them the photoalignment method is the most promising and intensively studied. Using this method, substrates are covered by photosensitive materials and subsequently irradiated with polarized UV or visible light (1,2). The photoalignment method allows simply controlling LC anchoring and easy axis direction in both azimuthal and polar planes. This makes possible patterned alignment used to ehhance viewing angles in nematic LCD. However, the photoaligning technique is usually accompanied with a low anchoring and relatively poor photo and thermal stability (3). Besides, LC alignment on the photoirradiated substrates is characterized by the pronounced image sticking effect which is a residual

image when the controlling voltage is changed (4).

From the first sight, the main problem of photoalignment is a problem of useful materials. However, following literature data, practically all photoaligning materials developed up to this date more or less suffer from the drawbacks mentioned above. This gives the reasons to conclude that shortcomings of photoalignment are mainly associated with treatment procedure. As we believe, the action of UV/V is light "softly" modifies aligning surface and so it is not capable to create strong boundary conditions for LC layers.

To overcome shortcomings of the conventional photoalignment method, M. Hazegava (5) suggested to use deep UV irradiation. He showed that 257 mn irradiation causes LC alignment effect on the polymers, which are non-sensitive to conventional UV/V is light. One more radical solution is suggested by Chaudhari et al. (6,7). It consists in oblique irradiation of the aligning polymer substrates with a collimated or partially collimated ion beam. This method provides excellent LC alignment on both organic (6,7) and non-organic (8-11) substrates. Later on, several modifications of the ion treatment method have been suggested. In (12) the aligning substrate is bombarded with ions at normal incidence in the presence of an electric field, which is applied in the area close to the substrate. In this case the applied field is sufficient to redirect ions obliquely to the substrate. The other modification is proposed in (13) where ion beam irradiation is used in combination with rubbing to produce two-domain pattering of the aligning substrate.

The advantages of deep UV irradiation and ion irradiation can be combined by the treatment of the aligning substrates with various kinds of plasma. The processing of LC substrates with the glow discharge was earlier applied for surface etching, grafting of the aligning surfaces with various atoms (14-17), as well as plasma polymerization (18-19). These processes

allowed to vary zenital anchoring energy and pretilt angle of LC. To generate LC alignment in-plane of the aligning substrates (azimuthal alignment), the substrates were preliminarily rubbed using conventional procedure. At the same time, planar and tilted LC alignment were not achieved using only plasma processing.

SUMMARY OF THE INVENTION

The present invention provides aligning substrates for uniform alignment of liquid crystals (planar, tilt and homeotropic) comprising organic and non-organic films treated with a collimated or partially collimated plasma beam.

The present invention also provides a method of making of aligning substrate comprising: providing a substrate and irradiating it with a collimated or partially collimated plasma beam. The incident angle of the plasma beam is crucial for the resulting type of alignment; titled irradiation produces planar and/or tilted homogeneous alignment. Normal (or perpendicular) irradiation often results in homeotropic alignment.

Plasma beam irradiation results in two types of easy axes (i.e. the direction of preferable molecular orientation): (1) an easy axis that is confined to the incident plane formed by the direction of the beam and the normal to the treated substrate; (2) an easy axis that is perpendicular to the plane of incidence. By increasing the irradiation dose one can change the alignment direction from the type (1) towards the type (2). In the first type of alignment, the value of the pretilt angle can be controlled with irradiation parameters (irradiation angle, ion current density, ion energy, etc.). The second type of alignment is characterized by a zero pretilt. Two-mode alignment feature can also be used to generate alignment with desirable parameters as well as to pattern LC cell.

The present invention also provides a class of plasma sources which can be used to generate uniform LC alignment. As an example of suitable plasma source, the anode layer thruster is proposed. The source can be easily designed to process large-area aligning substrates.

DETAILED DESCRIPTION OF THE INVENTION

FIGS. 1a through 1d show a schematic of the plasma source, profile of the discharge channel, and sample positions with respect to plasma beam.

FIG. 2 shows plasma current versus gas (Ar) pressure curves for various values of ion energy.

Figure 3a shows photos of combined cells having rubbed polyimide substrate as a reference substrate and plasma treated PVCN (polyvinyl cinnamate) substrate as an object substrate. The object substrates are irradiated in geometry 1 (FIG. 1c). The plasma irradiation parameters are $\alpha=60°$, $E=600$ eV, $\tau_{exp}=2.5$ min. The ion current density j is varied; j = 1, 2, 6, 8 and 25 $\mu A/cm_2$ in the cells 1, 2, 3, 5, and 5, respectively. The cells are 20 μm thick. They are filled with LC K15 (4-cyano-4'-pentyl-1,1'-biphenylene). The cells are placed between pair of crossed polarizers. The pictures demonstrate alignment mode 1 in cells 1 and 5, and alignment mode 2 in cells 2-4.

Figure 3b presents the azimuth angle of the direction of LC alignment as a function of current density of Ar^+ ions, starting from the direction of the incident plasma plane designated as 0° and rotate either clockwise or counterclockwise to 90°.

Figure 4 presents azimuth angle of the direction of LC alignment as a function of irradiation time for the following plasma treated aligning substrates: PVCN, PI (polyimide), PMMA (polymethyl methacrylate) (curve 1), PEMA (polyethyl methacrylate) (curve 2). The said substrates are irradiated at the following conditions: $\alpha=60°$, $E=600$ eV, $j=8$ $\mu A/cm^2$.

Figure 5 presents photos of two combined cells having rubbed PI substrate as a reference substrate and plasma glass slide as an object substrate. The object substrates are irradiated in geometry 1 (FIG. 1c) through the mask opening square area in the middle of the substrate. The irradiation parameters for cell 1 and cell 2 are $\alpha=70°$, E=400 eV, j=0.5 $\mu A/cm^2$, $\tau_{exp}=2.5$ min and $\alpha=70°$, j=6 $\mu A/cm^2$, E=500 eV, $\tau_{exp}=5$ min, respectively. The cells are 20 μm thick. They are filled with LC K15. The cells are placed between pare of crossed polarizers. The photos exhibit alignment mode 1 in the cell 1 and alignment mode 2 in the cell 2.

Figure 6 shows symmetrical cells based on plasma treated PI substrates viewed through crossed polarizers. Treatment parameters $\alpha=60°$, j=8 $\mu A/cm^2$, E=600 eV, and $\tau_{exp}=2.5$ min correspond to alignment mode 1. The substrates are combined to obtain parallel alignment (cell 1) and twist alignment (cell 2). Cell gap is 20 μm.

Figure 7 shows LC pretilt angle vs plasma incidence angle curves for different substrates; o- PVCN, □-PI, ∇ - PMMA, Δ - glass. The irradiation parameters for polymer and glass substrates are j=8 $\mu A/cm^2$, E=600 eV, $\tau_{exp}=2.5$ min and j=0.5 $\mu A/cm^2$, E=400 eV, $\tau_{exp}=2.5$ min respectively. The cells gap is 20 μm.

Figure 8 shows pretilt angle as a function of ion current density for PI substrate. The substrates are irradiated at the following conditions: $\alpha=60°$; E=600 eV, $\tau_{exp}=2.5$ min respectively.

Figure 9 demonstrates light transmission versus applied voltage curves for twist cells made of rubbed polyimide (□) and plasma beam treated polyimide (•) substrates. Plasma irradiation parameters: E=600V, J=8 $\mu A/cm^2$, $\tau_{exp}=2.5$ min, $\alpha=20°$). Thickness of both cells is 6 0.2 μm.

Figure 10 shows combined LC cell viewed between a pair of crossed (a) and parallel (b) polarizers. The cell is made of rubbed PI substrate and plasma treated PVCN substrate. The latter substrate is two-step irradiated

with plasma beam in geometry 1 (FIG. 1c); at first the substrate is entirely irradiated at $\alpha=70°$, $E=600V$, $j=8\ \mu A/cm^2$, $\tau_{exp}=2.5$ min (mode 1), then at $\alpha=70°$, $E=600V$, $j=8\ \mu A/cm^2$, $\tau_{exp}=5$ min (mode 2) through the mask. Two plasma treatment steps generate mutually perpendicular directions of LC alignment.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method of uniform (planar, tilted and homeotropic) alignment of LCs. The method operates with collimated or partially collimated plasma beams used to treat LC aligning substrates.

The materials that can function as aligning films in the present invention, which are cross-linked, degraded or etched by the collimated or partially collimated plasma, can be of organic and non-organic origin. The class of organic materials includes, but is not limited to, photosensitive such as poly(vinyl cinminate), or various unsaturated polyesters, and non-photosensitive polymers. Such polymers desirably have a high Tg such as at least about 100°C and preferably at least 150°C. Suitable examples of non-photosensitive include polyimide, various polyacrylates and methacrylates such as polymethyl methacrylate or polyethyl methacrylate, polyvinyl acetate, and the like. The class of non-organic materials comprises, but is not limited to, glass, quartz, gold, indium tin oxide (ITO), hydrogenated diamond-like carbon (DLC), and hydrogenated amorphous silicon. The films can be deposited on the substrate by any method as known to the literature and to the art. Suitable examples of depositing the organic films are spin coating and dip coating. For spin coating and deep coating, proper solvent should be used capable to dissolve the organic material. The methods suitable for depositing the non-organic films are thermal sputtering, plasma sputtering, etc.

The substrate upon which the film is contained can be any material commonly used for fabricating liquid crystal cells. Materials such as glass, quartz or plastic such as polyether sulfone (PES), polycarbonate (PC), polyethylene terephthalate (PET), or triacetate cellulose (TAC) can be used. The substrate materials can also be any materials commonly used for fabricating chips, for example silicon.

To treat the aligning film, any type of plasma source producing collimated or partially collimated beam of plasma can be employed such as those known to the art and to the literature. The gaseous feed used to excite plasma include, but are not limited to, Ar, O_2, N_2, CF_4. Conventional collimated or partially collimated plasma beams can be utilized to generate all types of uniform LC alignment described above. Plasma generators are known to the art and to the literature and generally any type thereof can be used. As a plasma source, an anode layer thruster specially designed to produce collimated or partially collimated plasma beams can be used. Compared with ion sources, the use of plasma sources for LC alignment has several advantages. First, the construction of plasma sources is much simpler than that of conventional ion sources. Second, the plasma beam (unlike an ionic beam) contains a number of components: ions, neutral atoms, electrons, protons, and deep UV (wavelength about less than 250 nanometers); this feature expands the aligning abilities of the technique, as not only the ions can be involved in the formation of the aligned substrates but other components too. For example, the deep UV irradiation accompanying the plasma beam can be used for additional photoalignment of the treated substrate. Third, the processing with the isotropic plasma previously utilized modify zenital alignment by the plasma-chemical treatment of the aligning substrates (grafting, polymerization, oxidation) can be replaced by the processing with collimated or partially collimated plasma beams to control both zenital and azimuthal alignment.

The plasma alignment technique of the present invention yields two different modes of alignment, with the resulting easy axis being either parallel or perpendicular to the incident plane, in contrast to the ionic beam techniques, which produce only one direction.

Homeotropic LC alignment can be generated by both oblique and normal incidence of the incidence of plasma flux. In the latter case, by the change of irradiation parameters (ion density and energy, irradiation time), two various alignment modes can be obtained. First of all, these modes differ by orientation of the induced easy axes (i.e., the direction of preferable orientation of LC molecules): 1) a first easy axis is confined to the incident plane formed by the direction of the beam and the normal to the treated substrate; 2) a second easy axis that is in the plane of film (perpendicular to the plane of incidence). By increasing the irradiation dose one can change the alignment direction from the type 1 to the type 2. For the alignment mode 1 (oblique incident of plasma flux), the value of the pretilt angle can be controlled with irradiation parameters (irradiation angle, ion current density, ion energy, etc.). The alignment mode 2 is characterized by a zero pretilt. Two azimuth alignment modes can be briefly described with the angles φ and θ introduced above the characterized uniform LC alignment. Assuming that azimuth angle φ is the rotational angle between projections of plasma beam and easy axis (long axis) of LC molecules on the substrate, one can summarize that, in case of the mode 1, $\varphi=0$, $\theta\geq0$, whereas, in case of the mode 2, $\varphi=90°$, $\theta=0$.

The two mode alignment feature is typical for organic and non-organic aligning layers, and it is observed for various kinds of LCs. The feature of two-mode alignment can be used to generate alignment with desirably parameters as well as to pattern LC cell.

It is an important fact that LC alignment preliminarily induced by plasma bean can be modified, or even overwritten, by subsequent plasma

irradiation steps. This feature, for instance, can be used to generate pretilt angle on the substrates preliminarily treated to align LCs in the mode 2. Also, the possibility to overwrite alignment reduces a number of masking processes used for cell patterning. Particularly, for two-domain alignment only one mask is required.

The plasma treatment suggested above can override alignment induced with other methods (e.g., rubbing, photoalignment, etc.). This means that plasma method may be successively combined with other methods for sample patterning.

The plasma treated alignment layer can be placed on one or both of the substrates in conventional liquid crystal cells. When the plasma treated layer is placed on only one of the substrates, any known alignment material may be placed on the remaining substrate. Other alignment materials include, but are not limited to, rubbed or light-irradiated polyimides, light-irradiated polyvinylcinnamate, oblique deposited SiO_x.

The LC alignment on plasma treated substrates is extremely photo and thermally stable. The photo and thermal stability are comparable with those for rubbing method.

The invention will be better understood by reference to the following description and examples which to serve to illustrate, but not to the limit the scope of the present invention.

The films of photosensitive and non-photosensitive polymers were used as organic aligning films. The films were obtained by spin coating polymer solution onto substrates such as bare glass or indium tin oxide (ITO) coated glass slides.

To treat the substrates, the following set up can be utilized wherein an anode layer plasma source such as an electrodynamic thruster was used which is known to the art and to the literature. This source is specially designed to produce a collimated or partially collimated flux of plasma from

practically any gaseous feed. The sketch of the anode layer thruster is shown in FIG. 1a. The source contains permanent magnets on the inner and outer cathodes C. The anode A is above the inner and outer cathodes. Together these electrodes define the size and the shape of the discharge channel. The ion flux is formed in crossed E and H fields immediately within the discharge channel and so it is a part of d.c. plasma generated in the discharge area. The sheet like plasma fluxes produced by the anode layer sources easily treats large-area substrates (using translation method). Additionally, the anode layer thrusters have simplified construction. In contrast to electrostatic thrusters, they do not require filaments or secondary electron sources to initiate discharge current or to neutralize the beam. Also, since ions are accelerated electrodynamically, the anode layer thrusters do not need grids to extract and accelerate ions.

The anode layer thruster with the race track shape of the discharge channel (see FIG. 1b) is mounted in vacuum chamber 1 (see FIG. 1a). The channel is elongated to produce sheet-like plasma beams. The chamber is pumped out up to pressure 10^{-5} Torr, and then is filled by argon. The working pressure p in our experiments was (2-10)10^{-4} Torr. The pressure of Ar determines current density j of the plasma ions Ar^{+}. The j versus p curves for various values of the anode potential U are presented in FIG. 2. The anode potential also determines ion energy E. The E was varied within 200-900 eV.

Substrate holders 3 and 5 are mounted in vacuum chamber 1 just under discharge channel 4 (FIG. 1a). A distance between plasma outlet and irradiated substrate is about 10 cm. The holder can be rotated to perform irradiation in geometry 1 (FIG. 1c), when the substrate is tilted in the direction perpendicular to plasma sheet; and geometry 2 (FIG. 1d), when the substrate is tilted in plane of the plasma sheet. The plasma beam incidence angle α can be varied within 0° and 85°. In addition to α, other

parameters of plasma irradiation can be varied: 1) irradiation time τ_{exp} from about 1 second to about 2 hours; 2) ion current density *j* from about 0.1 to about 100 $\mu A/cm^2$; and ion particle energy *E* from about 10 to about 2,000 and desirably from about 200 to about 400 eV.

Two kinds of LC cells were prepared: 1) one substrate is irradiated by plasma beam, while the second one is a rubbed polyimide layer (combined cells); and 2) with both substrates irradiated by plasma beam (symmetrical cells). To get an antiparallel director configuration, the irradiation directions were antiparallel. The cell gap was maintained with spacers of 6 µm and 20 µm in diameter. The cells were filled with nematic LC K15 (5CB) and ZLI 4801-000. The symmetrical cells were used to determine pretilt angle of LC by crystal rotation technique. Using combined cells direction of LC azimuthal alignment has been estimated. In addition, these cells were used to estimate azimuthal anchoring energy connected with the twist angle of LC experimentally measured.

The examples presented below illustrate abilities of the suggested technique and properties of the obtained alignment of LCs. The examples are divided into 3 groups; the first group (examples 1.1 – 1.17) demonstrates possibilities to generate various alignment modes, the second group (examples 2.1 – 2.17) is focused on control of alignment parameters (pretilt angle, anchoring energy, etc.), and the third one (example 3.1-3.3) considers the method of cell patterning.

Example 1.1

The polyvinylcinnamate photosensitive polymer film from Aldrich is dissolved in dichloroethane (weight concentration of 20 g/l). A droplet of this solution is deposited on a rectangular glass substrate (2x3 cm) containing ITO electrode and spin-coated for 30 seconds at 2500 rpm. Then the substrate is

maintained for 2 hours at 90°C to remove the solvent. As a result, a uniform polymer film is produced.

The substrate coated with PVCN (Polyvinyl cinnamate) film is subjected to plasma irradiation in geometry 1 (FIG. 1c). The irradiation parameters are as follows: plasma incidence angle $\alpha = 70°$, ion current density $j = 1\ \mu A/cm^2$, ion energy $E = 600$ eV, irradiation time $\tau_{exp} = 5$ min.

The combined cells is prepared in which aligning layers are, respectively, plasma treated layer (object substrate) and rubbed polyimide layer (reference substrate). The rubbing direction corresponds to a long side of the rectangular substrate. The cell with a gap of 20 µm is prepared and filled with LC K15. The picture of this sample is crossed polarizers is presented in FIG. 3a (picture 1). The dark color of the cell shows that azimuthal alignment direction on the object substrate is parallel to the rubbing direction on the reference substrate. This implies that the alignment direction on the plasma treated substrate is confined to the incidence plane of plasma beam. This type of alignment we define as alignment mode 1.

Example 1.2

A combined cell is prepared as in Example 1.1 except the cells are filled with LC ZLI 4801. The obtained alignment of LC corresponds to alignment mode 1.

Example 1.3

A series of combined cells (5 cells) is prepared. The cell preparation process is as in Example 1 except the value of current density j of plasma ions is varied ($j = 1, 2, 6, 8, 12, 25\ \mu A/cm^2$). The pictures of the obtained samples are presented in FIG. 3a (pictures 1, 2, 3, 4, and 5, correspondingly). The white area in the cells 2-4 corresponds to central

part of the plasma beam, whereas black area to the periphery part of the beam. The alignment in the black area corresponds to alignment mode 1, while the alignment in the white area corresponds to the new type of alignment. The LC easy axis in the white area is oriented perpendicularly to rubbing direction on the reference substrate. This means that the easy axis is induced perpendicularly to the plane of the plasma beam incidence. This type of alignment we define as alignment mode 2. The azimuth angle of the easy axis on the plasma treated substrate φ (the angle between projection of plasma beam and LC easy axis on the plane of substrate) as a function of j is presented in FIG. 3b. The threshold-like transition from the mode 1 to the mode 2 is realized in the relatively narrow range of the current density of plasma ions (2 $\mu A/cm^2 < j < 12$ $\mu A/cm^2$).

Example 1.4

A series of combined cells is prepared as in Example 1.1 except the object substrates are treated with plasma beam in geometry 2 (see FIG. 1c). The LC alignment results are same as in Example 1.3

Example 1.5

A series of combined cells (8 cells) is prepared. The cell preparation process is as in Example 1.1 except that irradiation time is varied (τ_{exp}=2.0, 3.0, 3.5, 4.5, 5, 6.5, 10, 15 min) and the ion current density is fixed (j=8 $\mu A/cm^2$). The pictures corresponding to τ_{exp}=2 min and τ_{exp}=10 min irradiation are presented in FIG. 4a (picture 1 and 2, respectively). The azimuth angle φ of the LC easy axis as a function of τ_{exp} is presented in FIG. 4b (curve 1). As one can see, the threshold-like transition from the alignment mode 1 to the alignment mode 2 is observed in the range 4 min$<\tau_{exp}<$5 min.

Example 1.6

A series of combined cells is prepared in Example 1.5 except the object substrates are treated with plasma beam in geometry 2 (see FIG. 1c). The φ vs τ_{exp} curve is same as in example 1.5 (curve 1 in FIG. 4b).

Example 1.7

A series of combined cells is prepared as in Example 1.5 except the object substrates contain polyimide (PI) aligning films. The films were prepared as follow. The 15 g/l solution of polyimide 2555 by Dupont was spin coated on the glass slides (2,500 rmp, 30 min). In the following the substrates were backed 10 min at 90°C and, subsequently, 2 h at 200°C. The φ vs τ_{exp} curve is same as in Example 1.5 (curve 1 in FIG. 4b).

Example 1.8

A series of combined cells is prepared as in Example 1.5, except the object substrates contain polymethylmethacrylate (PMMA) aligning films. The films are prepared as follow. The 10 g/l solution of PMMA by Aldrich is spin coated on the glass slides. In the following the substrates are backed 2 h at 150°C. The dependence of the azimuth angle of the LC easy axis on the exposure time τ_{exp} is the same as in Example 1.5 (curve in FIG. 4b).

Example 1.9

A series of combined cells is prepared as in Example 1.5 except the objection substrates contain polyethylmethacrylate (PEMA) aligning films. The films are prepared as follows. The 10 g/l solution of PS by Aldrich is spin coated on the glass slides. In the following the substrates are backed 2 h at 150°C. Same as in Example 1.5 the transition form alignment mode 1 to alignment mode 2 is observed with the increase of τ_{exp}. However, compared with PVCN, PI, and PMMA, the transition realizes at higher values of τ_{exp}.

Example 1.10

The PVCN aligning film on the glass slide is prepared as in Example 1.1. The film is treated with plasma beam at the parameters corresponding to aligning mode 1: $\alpha=60°$, $j=8$ $\mu A/cm^2$, $E=600$ eV, $\tau_{exp}=2.5$ min.

The cell is prepared as in Example 1.1, except that the substrates are combined so that 90° twist LC alignment is obtained (irradiation direction of the object substrate is perpendicular to rubbing direction of the reference substrate). The azimuth anchoring energy on the plasma treated substrate is estimated to be about 10^{-3} erg/cm^2.

Example 1.11

The PVCN aligning coating on the glass slide is prepared as in Example 1.1. The film is treated with plasma beam at the parameters corresponding to aligning mode 2: $\alpha=60°$, $j=8$ $\mu A/cm^2$, $E=600$ eV, $\tau_{exp}=2.5$ min.

The cell is prepared as in Example 1.1, except that the substrates are combined so that 90° twist LC alignment is obtained (irradiation direction of the object substrate is perpendicular to rubbing direction of the reference substrate). The azimuth anchoring energy on the plasma treated substrate is estimated to be about 10^{-3} erg/cm^2.

Example 1.12

The bare glass substrate (microscope slide from Fisher Schientific) is irradiated in a geometry 1 (FIG. 1c) at the following conditions: $\alpha=70°$, $j=0.5$ $\mu A/cm2$, $E=400$ eV, $\tau_{exp}=2.5$ min. The substrate is irradiated through the mask from aluminum foil, which opens only central part of the substrate.

The combined cell is prepared as in Example 1.1. The picture of this sample in crossed polarizers is presented in FIG: 5a. As can be seen, alignment mode 1 is realized in the irradiated area (black square in the middle of the cell).

Example 1.13

The bare glass substrate (microscope slide from Fisher Scientific) is irradiated in a geometry 1 (FIG. 1c) at the following conditions: $\alpha=70°$, $j=6$ $\mu A/cm^2$, $E=500$ eV, $\tau_{exp}=5$ min. The substrate is irradiated through the mask from aluminum foil, which opens only central part of the substrate.

The combined cell is prepared as is described in Example 1.1. The picture of this sample in crossed polarizes is presented in FIG. 5b. The alignment mode 2 is realized in the plasma irradiated area (white square in the middle of the cell).

Example 1.14

The combined cell is prepared as in Example 1.12, except that the object substrate is ITO covered glass slide. Same as in Example 1.12, alignment mode 1 is realized.

Example 1.15

The combined cell is prepared as in Example 1.13, except that the object substrate is ITO covered glass slide. Same as in Example 1.12, alignment mode 2 is realized.

Example 1.16

The combined cell is prepared as in Example 1.12, except that the object substrate is a bare quartz slide and the cell is filled with LC ZLI 4801. The alignment mode 1, same as in Example 1.11, is realized.

Example 1.17

The combined cell is prepared as in Example 1.13, except that the object substrate is a bare quartz slide and the cell is filled with LC ZLI 4801. The alignment mode 2, same as in Example 1.12, is realized.

Example 2.1

Two films of polyimide 2555 (Dupont) on the glass substrates are prepared as in Example 1.7. These films are subjected to plasma irradiation in geometry 1 (FIG. 1c). The irradiation parameters are: $\alpha=60°$, $j=8\ \mu A/cm^2$, $E=600$ eV, $\tau_{exp}=2.5$ min. Following Example 1.7, these parameters correspond to generation of the alignment mode 1.

The substrates are used to prepare symmetrical cell: To get an antiparallel director configuration in the cell, the irradiation directions are antiparallel. The cell gap is 20 μm. The cell is filled with LC K15. The picture of this cell in crossed polarizers is presented in FIG. 6 (photo 1). LC director is tilted towards direction of irradiation. The value of pretilt angle of the LC is determined to be 5.5°C.

Example 2.2

The symmetric cell is prepared as in Example 2.1 except that substrates are irradiated in geometry 2 (FIG. 1c). Same as in Example 2.1, LC director is tilted towards direction of irradiation. The value of LC pretilt angle is about 5°.

Example 2.3

The PI coated substrates are prepared and treated as in Example 2.1. The symmetrical cell with the twisted director configuration is prepared. For this purpose the substrates are combined so that irradiation directions are perpendicular. The picture of this cell in crossed polarizers is presented in FIG. 6 (photo b).

Example 2.4

A series of symmetric cells is prepared as in Example 2.1, except that incidence angle is varied; α =0°, 10°, 20°, 30°, 40°, 50°, 60°, 70°, 80°. The

uniform alignment is achieved for α = 20° - 80°. The θ versus α curve is shown in FIG. 7.

Example 2.5

A series of symmetric cells is prepared as in Example 2.4 except that aligning substrates are covered by PVCN films prepared as in Example 1.1. The uniform alignment is achieved for θ = 20° - 80°. The θ versus α curve is shown in FIG. 7.

Example 2.6

A series of symmetric cells is prepared as in Example 2.4 except that aligning substrates are covered by PMMA films prepared as in Example 1.8. The uniform alignment is achieved for θ = 20° - 80°. The versus α curve is shown in FIG. 7.

Example 2.7

A series of symmetric cells is prepared as in Example 2.4 except that aligning substrates are bare glass substrates (Fisher Scientific) treated as in Example 1.11, except that incidence angle is varied; θ=0°, 10°, 20°, 40°, 50°, 60°, 70°, 80°. The uniform alignment is achieved for θ = 30° - 80°. The θ versus α curve is shown in FIG. 7.

Example 2.8

The bare glass substrates (Fisher Scientific) are treated with plasma at the following conditions: α=60°C, j=8 $\mu A/cm^2$, E=600 eV, τ_{exp}=5 min. The symmetric cell is assembled as in Example 2.1. The cell is filled with LC K15. Homeotropic LC alignment in the cell is observed.

Example 2.9

The sample is prepared as in Example 2.8, except substrates are irradiated at normal incidence of plasma beam. Homeotropic LC alignment in the cell is observed.

Example 2.10

The sample is prepared as in Example 2.8, except the substrates are bare slides of quartz. Homeotropic LC alignment in the cell is observed.

Example 2.11

A series of symmetric cells is prepared as in Example 2.1, except that ion current density j is varied; $j = 2.5$, 8, 20, and 35 $\mu A/cm^2$. The θ versus j curve is shown in FIG. 8.

Example 2.12

PVCN substrates are prepared as in Example 1.1 and treated with plasma in geometry 1 at the parameters: $\alpha = 60°C$, $j = 8\ \mu A/cm^2$, $E = 600$ eV, $\tau_{exp} = 5$ min. Following Example 1.5, the irradiation conditions correspond to the alignment mode 2. By cell assembling the substrates are combined so that directions of plasma irradiation are antiparallel. The thickness of the cell is 20 μm. The cell is filled with LC K15. The tilt angle of LC in the cell is about 0.

Example 2.13

The symmetric cell is prepared as in Example 2.11, except that substrates are combined so that directions of plasma irradiation are parallel. The tilt angle of LC K15 in the cell is about 0.

Examples 2.12 and 2.13 show that pretilt angle of LC K15 on PVCN substrates in case of alignment mode 2 is 0.

Example 2.14

Two symmetric cells are prepared as in Example 2.12 and Example 2.13, respectively. The cells are filled with LC ZLI 4801. The crystal rotation studies show that pretilt angle of LC is about 0.

Example 2.15

Two symmetric cells are obtained as in Example 2.12 and Example 2.13, respectively, except the substrate are irradiated in geometry 2. The crystal rotation studies show that pretilt angle of LC is about 0.

Example 2.16

Two polyimide substrates are prepared as in Example 1.7. The films are irradiated at $\alpha=60°C$, $j=8$ $\mu A/cm^2$, $E=600$ eV, $\tau_{exp}=10$ min and, subsequently, at $\alpha=60°C$, $j=8$ $\mu A/cm^2$, $E=600$ eV, $\tau_{exp}=2$ min. After the first irradiation step the substrates are rotated so that the second direction of plasma irradiation is perpendicular to the first one. Using these substrates symmetric cell is prepared. By cell assembling the substrates are combined so that directions of the second plasma irradiation are antiparallel. The thickness of the cell is 20 µm. The cell is filled with LC K15. Tilted alignment of LC is observed. LC director is tilted towards direction of second irradiation. The value of pretilt angle is about 3.5°.

Example 2.17

Two polyimide films are prepared as in Example 1.7. The films are irradiated at the following conditions; (1): $\alpha=60°C$, $j=8$ $\mu A/cm^2$, $E=600$ eV, $\tau_{exp}=2$ min, and (2) $\alpha=60°C$, $j=8$ $\mu A/cm^2$, $E=600$ eV, $\tau_{exp}=10$ min. Using these substrates symmetric cell is prepared. By cell assembling the substrates are combined so that directions of plasma beam incidence are

antiparallel. The thickness of the cell is 20 μm. The cell is filled with LC K15. Twist alignment of LC in the cell (twist angle about 90°) is observed.

Example 2.18

Two polyimide substrates are prepared as in Example 1.7. The films are irradiated at the following conditions: $\alpha=60°C$, $j=8\ \mu A/cm^2$, $E=600$ eV, $\tau_{exp}=10$ min. Using these substrates symmetric cell is prepared. By cell assembling the substrates are combined so that incidence directions of plasma beam are mutually perpendicular. The thickness of the cell is 6 μm. The cell is filled with LC K15. Twist alignment of LC in the cell (twist angle about 90°) is observed. The cell is placed between parallel polarizers and subjected to alternative electric field (sine-like signal, f=1 kHz). The trasmittance versus voltage curve is presented in FIG. 9 (curve 1).

Curve 2 in FIG. 9 corresponds to other cell. The cell is prepared as previous one except polyimide films are subjected to rubbing instead of plasma irradiation. Curves 1 and 2 are very similar. Thus, the cells based on plasma alignment and rubbing alignment show identical electrooptic performance.

Practically all methods of the cell patterning known for photoalignment and ion beam alignment technique can be applied for the plasma beam alignment. We consider below only several additional methods based on possibility to induce various alignment modes.

Example 3.1

Polyvinylcinnamate film on the glass substrate (3x2 cm) is prepared as in Example 1.1. The film is irradiated in geometry 1 at the following parameters: $\alpha=70°C$, $j=8\ \mu A/cm^2$, $E=600$ eV, $\tau_{exp}=2$ min. The irradiation conditions correspond to induction of the alignment mode 1. Then the film is covered with aluminum mask and irradiated again without change of the

sample position. The irradiation parameters of the second irradiation are $\alpha = 70°C$, $j = 8\ \mu A/cm^2$, $E = 600$ eV, $\tau_{exp} = 10$ min. They correspond to alignment mode 2.

The combined cell is prepared from the said plasma treated substrate and rubbed PI substrate. Rubbing direction of the rubbed substrate is antiparallel to the plasma irradiation direction of the plasma treated substrate. The cell gap is 20 μm. The cell is filled with LC K15. The picture of this cell is shown in FIG. 10. One can see alignment domains with mutually perpendicular directions of easy axis in the azimuth plane.

Example 3.2

The cell is prepared as in Example 3.1 except the first plasma treatment is replaced by irradiation with UV light from mercury lamp. The light polarized by Glan polarizing prism is directed normally to the substrate. The light polarization corresponds to the long side of the substrate. The light intensity and irradiation time are 12 mW/cm^2 and 15 min, respectively. Same as in Example 3.1, the alignment domains with mutually perpendicular directions of easy axis in the azimuth plane are observed.

The liquid crystals utilized are conventional and known to the art. Desirably they are nematic liquid crystals which are generally characterized by a rod-like appearance of a single component or commercially available eutectic mixture. Alternatively, ferroelectric liquid crystals can be utilized such as those optically-active single components, exhibiting a smectic C phase with tilted layer structure.

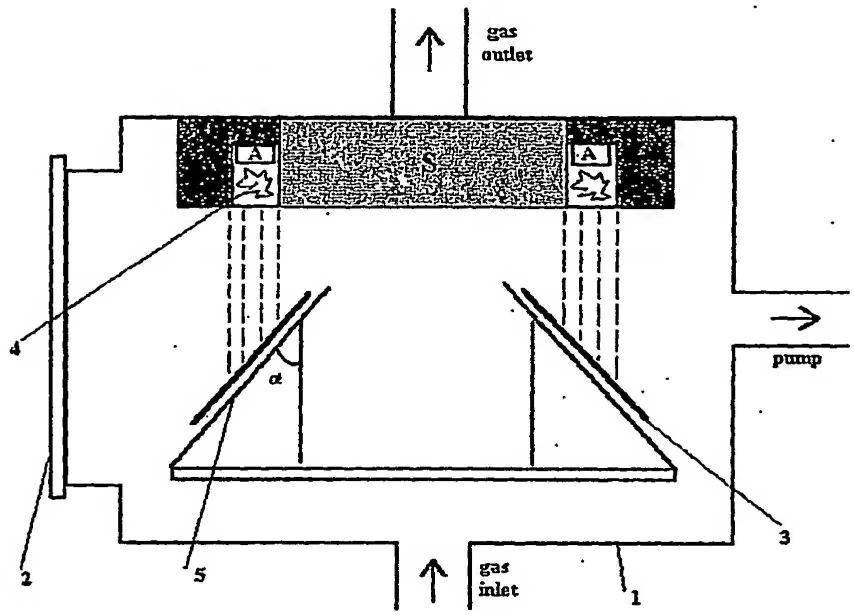
WHAT IS CLAIMED IS:

1. A process for aligning liquid crystals, comprising the steps of:

irradiating a substrate containing liquid crystals thereon with a collimated or partially collimated plasma beam, and

substantially aligning said liquid crystals in a homeotropic, tilted, or planar alignment, or combinations thereof.

DRAWINGS



1- vacuum chamber
2 – window
3,5 – sample holder
4 – glow discharge

Fig.1 a

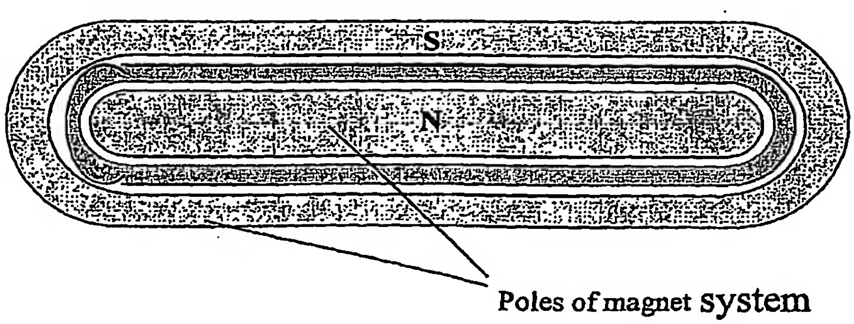


Fig. 1 b

60471717 .051903

1

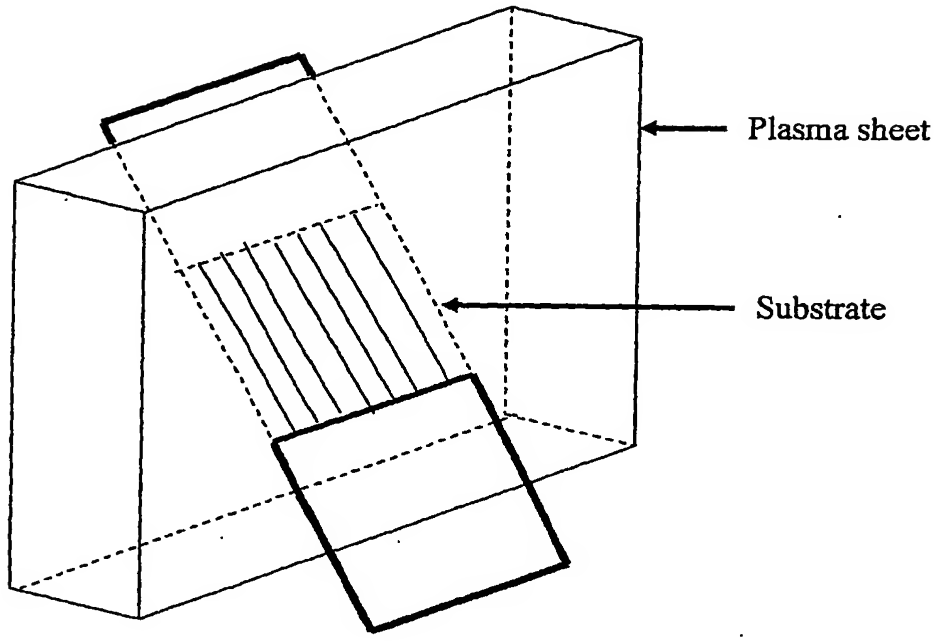


FIG 1c

2

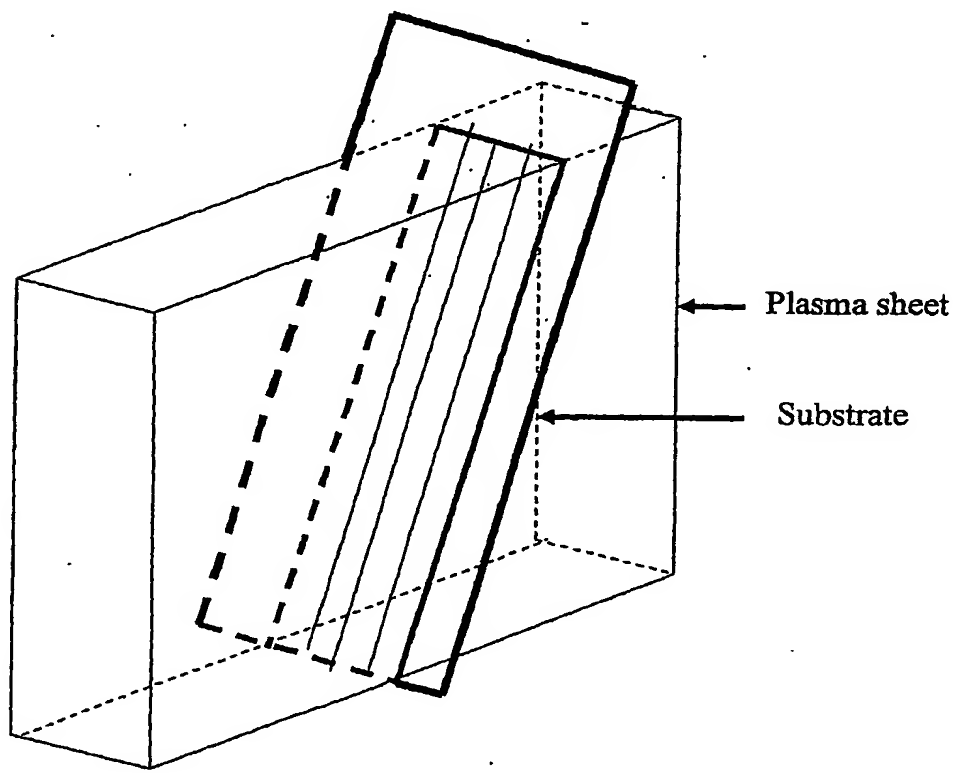
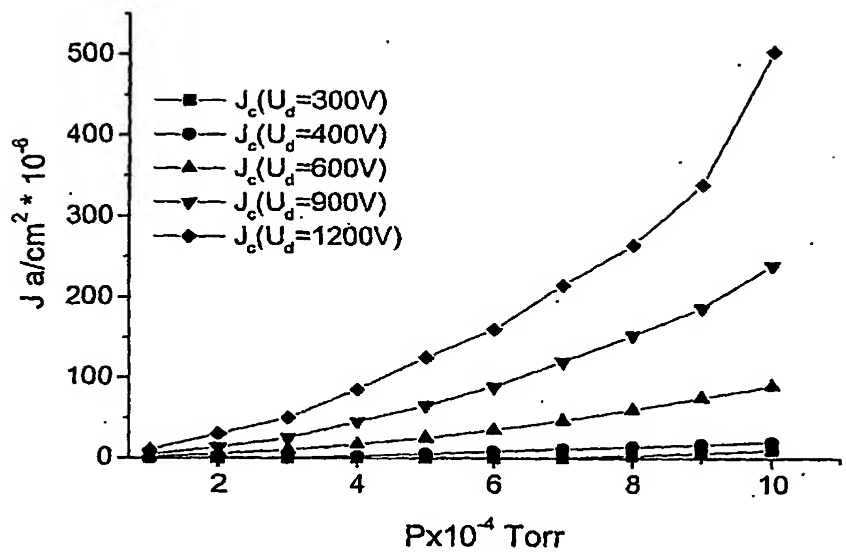


Fig. 1 d



500
400
300
200
100
0
2
4
6
8
10
J a/cm² * 10⁻⁶
Px10⁻⁴ Torr
J_c(U_d=300V)
J_c(U_d=400V)
J_c(U_d=600V)
J_c(U_d=900V)
J_c(U_d=1200V)

Fig. 2.

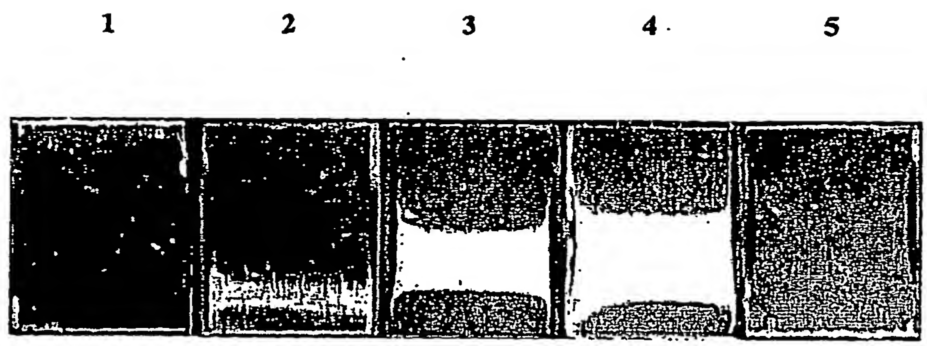


Fig. 3 a

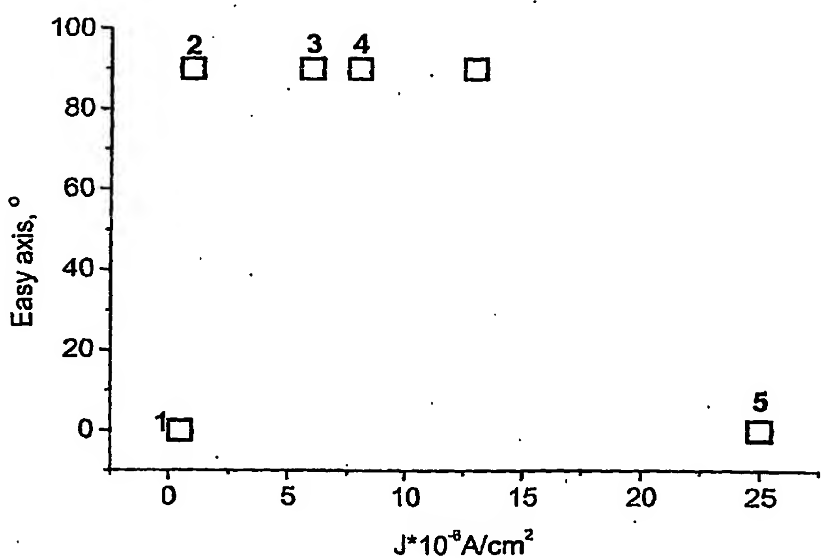


Fig. 3 b

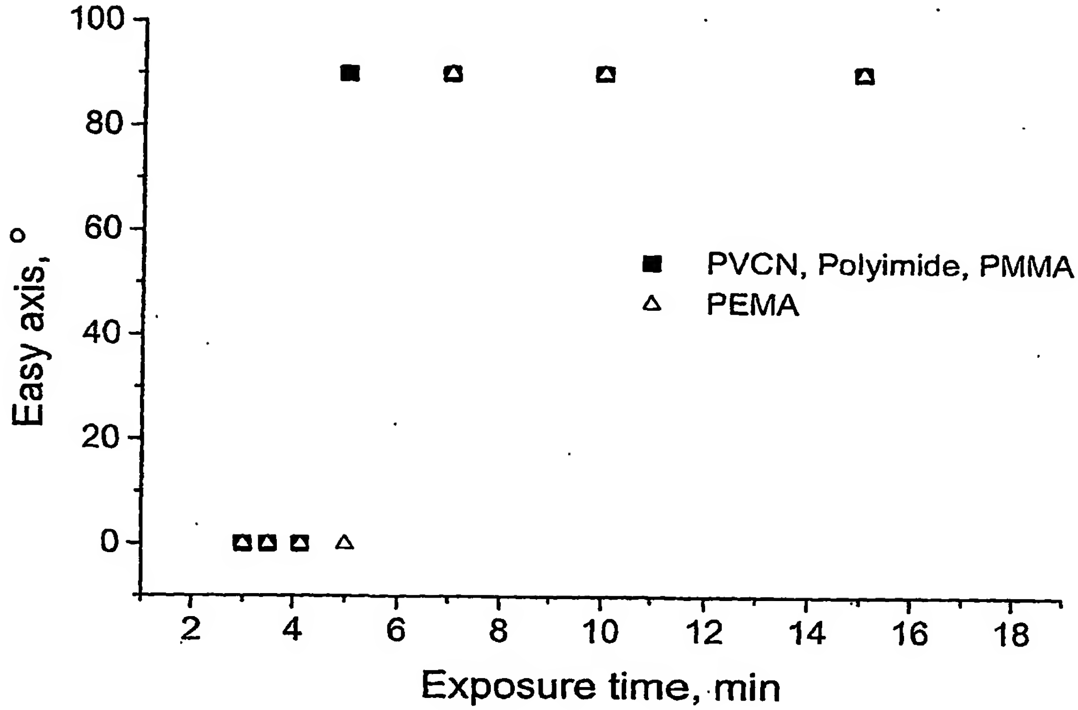
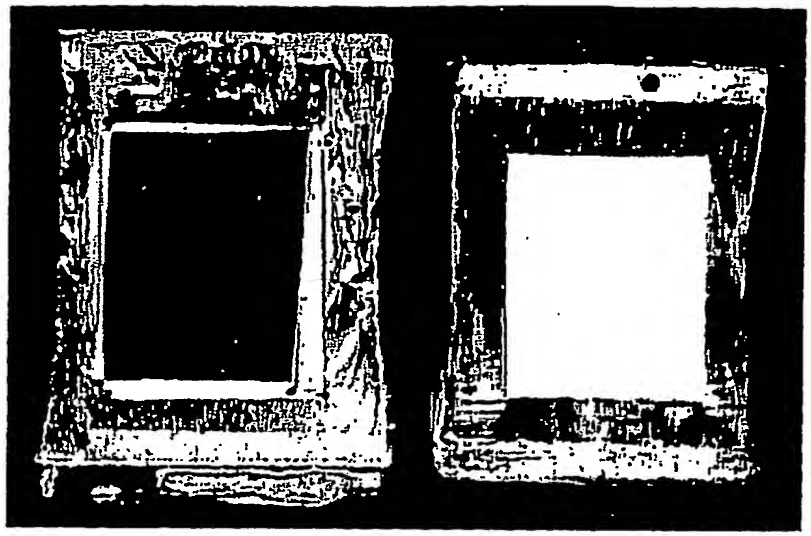
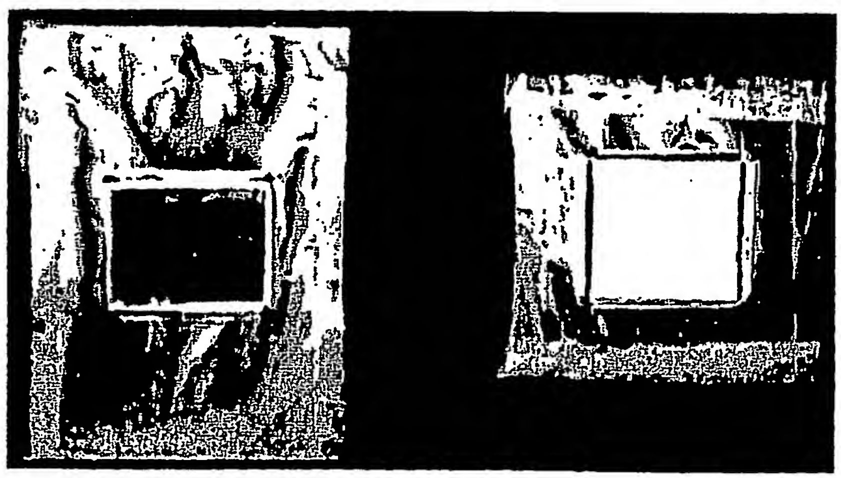

100
80
60
40
20
0
Easy axis, °
2
4
6
8
10
12
14
16
18
Exposure time, min
PVCN, Polyimide, PMMA
PEMA

Fig. 4



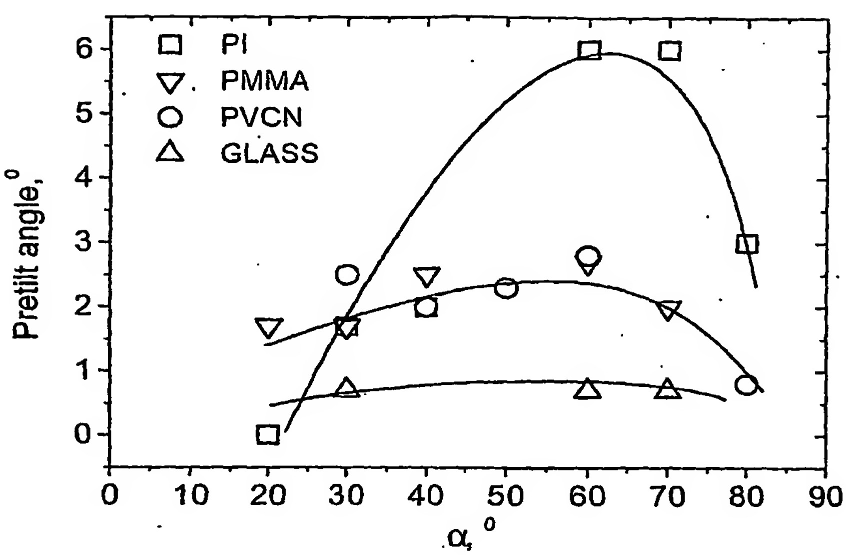
a b

Fig. 5



a b

Fig. 6



PI
PMMA
PVCN
GLASS
Pretilt angle, °
α, °
0
1
2
3
4
5
6
0
10
20
30
40
50
60
70
80
90

Fig. 7

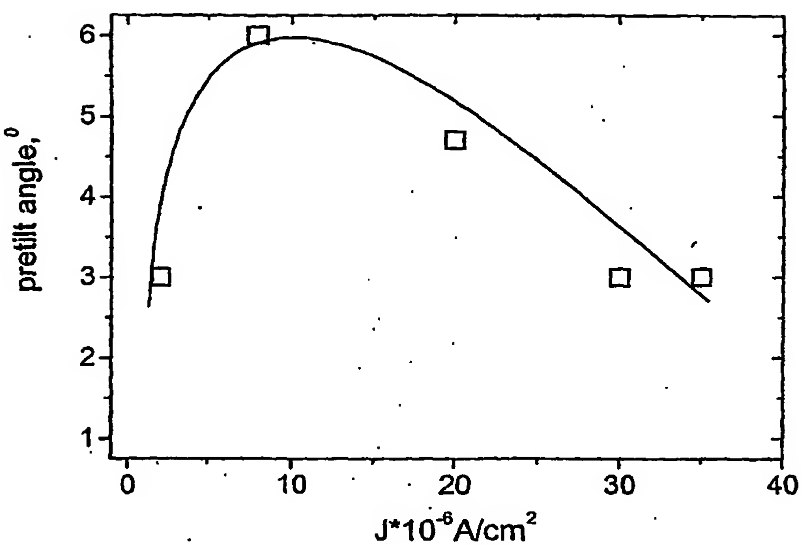


Fig. 8

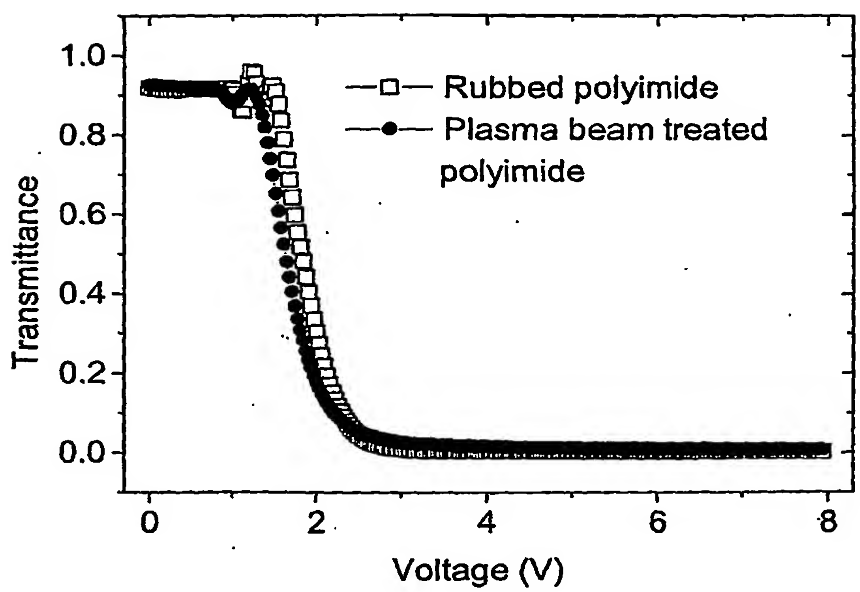

1.0
0.8
0.6
0.4
0.2
0.0
Transmittance
0
2
4
6
8
Voltage (V)
Rubbed polyimide
Plasma beam treated polyimide

Fig. 9

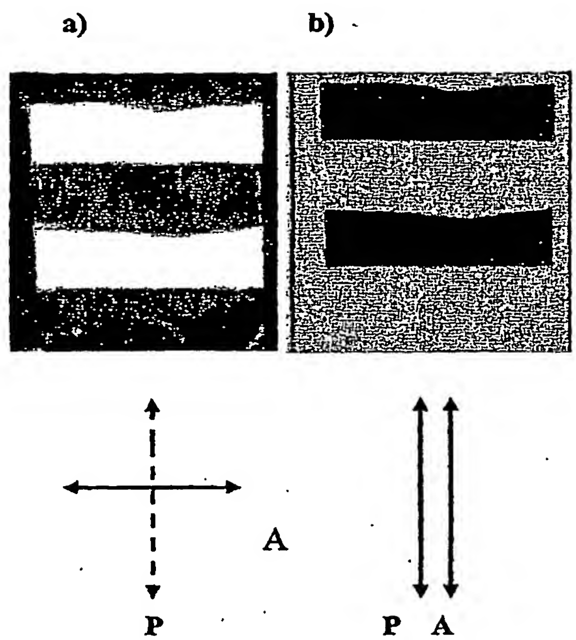


Fig. 10